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N-Octanol/Water Partition Coefficients by Reverse Phase Liquid Chromatography/Mass Spectrometry for Eight Tetrachlorinated Planar Molecules

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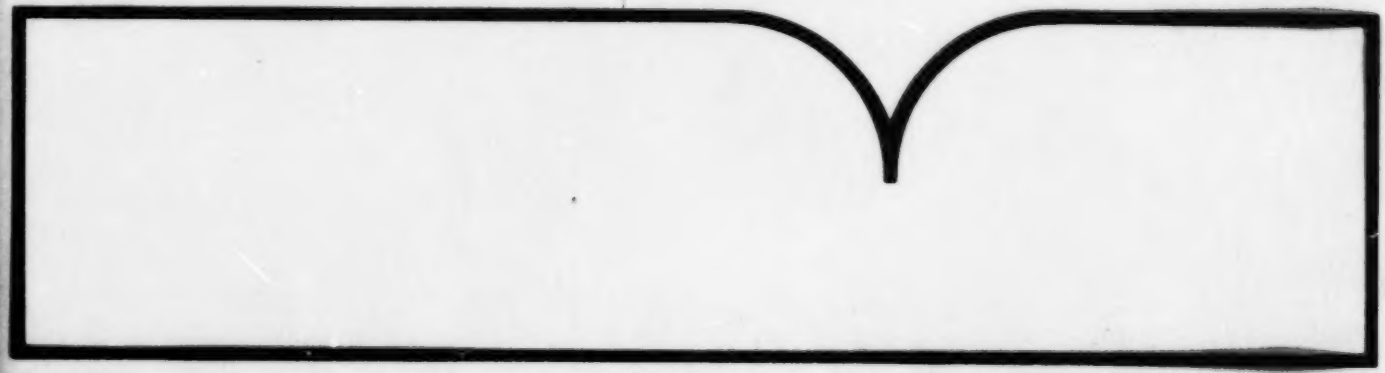

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16. ABSTRACT

N-octanol/water partition coefficients (K_{ow}'s) were determined using reverse phase liquid chromatography for eight tetrachlorinated planar molecules. The log K_{ow}'s are as follows: 2,3,7,8-, 1,2,3,4-, 1,3,7,9-, and 1,3,6,8-tetrachlorodibenzo-p-dioxins, 7.02, 7.18, 7.06, and 7.20, respectively; 2,3,7,8-tetrachlorodibenzofuran, 5.82; 1,3,6,8-tetrachloro-9H-carbazole, 5.75; 2,3,6,7-tetrachlorobiphenylene, 6.14; and 3,3',4,4'-tetrachlorobiphenyl, 5.81. The accuracy of these values was estimated to be ca. ± 0.50.

Reevaluation of log K_{ow}'s previously determined using reverse phase liquid chromatography for chlorinated dibenzofurans and dibenzo-p-dioxins yielded values of ca. 7.0 for the tetrachlorodibenzo-p-dioxins. also. This reevaluation was performed by using experimental rather than estimated log K_{ow}'s in the correlative relationship. In addition, these values suggest that the log K_{ow}'s for dibenzo-p-dioxins and dibenzofurans range from ca. 4.0 for the unsubstituted parent molecule to ca. 8.6 for the octachlorinated compounds; much lower than previously reported.

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N-OCTANOL/WATER PARTITION COEFFICIENTS BY REVERSE PHASE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY FOR EIGHT TETRACHLORINATED PLANAR MOLECULES

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ABSTRACT

N-octanol/water partition coefficients (K_{ow}'s) were determined using reverse phase liquid chromatography for eight tetrachlorinated planar molecules. The log K_{ow}'s are as follows: 2,3,7,8-, 1,2,3,4-, 1,3,7,9-, and 1,3,6,8-tetrachlorodibenzo-p-dioxins, 7.02, 7.18, 7.06, and 7.20, respectively; 2,3,7,8-tetrachlorodibenzofuran, 5.82; 1,3,6,8-tetrachloro-9H-carbazole, 5.75; 2,3,6,7-tetrachlorobiphenylene, 6.14; and 3,3',4,4'-tetrachlorobiphenyl, 5.81. The accuracy of these values was estimated to be ca. $\pm$ 0.50.

Reevaluation of log K_{ow}'s previously determined using reverse phase liquid chromatography for chlorinated dibenzofurans and dibenzo-p-dioxins yielded values of ca. 7.0 for the tetrachlorodibenzo-p-dioxins. also. This reevaluation was performed by using experimental rather than estimated log K_{ow}'s in the correlative relationship. In addition, these values suggest that the log K_{ow}'s for dibenzo-p-dioxins and dibenzofurans range from ca. 4.0 for the unsubstituted parent molecule to ca. 8.6 for the octachlorinated compounds; much lower than previously reported.

INTRODUCTION

In understanding and modeling the toxicological and pharmacokinetic properties of organic chemicals, physical-chemical properties such as aqueous solubilities, vapor pressures, and n-octanol/water partition coefficients are required. Currently, the octanol/water partition coefficients (K_{ow}'s) are limited for chlorinated planar molecules, e.g., dibenzo-p-dioxins, dibenzofurans, biphenylenes, and carbazoles. In this paper, log K_{ow}'s determined using a reverse phase liquid chromatography/mass spectrometry technique (1) are reported for eight tetrachlorinated planar molecules. In addition, we report

a reevaluation of log K_{ow}'s for fifteen polychlorinated dibenzofurans and dibenzo-p-dioxins previously reported by Sarna et al. (2). This reevaluation was performed by using experimental rather than estimated log K_{ow}'s in the correlative relationship.

EXPERIMENTAL

Compounds and Reagents: 2,3,7,8-tetrachlorodibenzofuran was obtained from Cambridge Isotope Laboratories (Woburn, MA). 1,3,6,8-, 1,3,7,9-, 1,2,3,4-, and 2,3,7,8-tetrachlorodibenzo-p-dioxins were obtained from US-EPA Dioxin Repository (US-EPA, EMSL, Las Vegas, NV). The tetra-, penta-, and deca-chlorobiphenyls were obtained from Analabs (North Haven, CT) and the di- and octa-chlorobiphenyls were obtained from Ultra Scientific (Hope, RI). All of the chlorinated benzenes were obtained from Aldrich Chemical (Milwaukee, WI). The 1,3,6,8-tetrachloro-9H-carbazole was synthesized inhouse previously (3) and the 2,3,6,7-tetrachlorobiphenylene was kindly provided by Dr. C. Rappe (University of Umea, Umea, Sweden). (The chlorine substitution on the tetrachlorobiphenylene is unconfirmed. However, mass spectrometry analyses indicate a $C_{12}Cl_8$ molecule.) All compounds were used as received. All chromatographic solvents were HPLC grade.

Instrumental: A Finnigan-Mat 4500 quadrupole mass spectrometer (San Jose, CA) equipped with an INCOS data system was used in electron impact or negative chemical ionization mode with multiple-ion-selection (MIS) mass analyses. Masses used to monitor for the eight planar molecules were the two largest ions in their respective molecular ion clusters. A 0.250 amu mass window was centered upon the exact mass of the ion for MIS. The liquid chromatography/mass spectrometry interface and the microbore high pressure liquid chromatography (HPLC) system have been described elsewhere (1).

Method: The HPLC column was operated at ambient temperature and with a flow rate of 0.10 mL/min. The solvent conditions were isocratic for 1.0 minute initially with 100% solvent A, then linearly programmed to 100% solvent B at a rate of 6.67%/min, and then isocratic for 30 minutes with 100% solvent B. A 10.0 minute recycle time was allowed between runs with 100% solvent A. Solvents A and B were composed of methanol, ethanol, and water at compositions of 70.0:15.0:15.0 and 94.0:5.0:0.0.

Seven chemicals with measured K_{ow}'s were used to correlate the elution time from the HPLC column to the K_{ow}'s. Compounds used were: chlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 4,4'-dichlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, 2,2',3,3',5,5',6,6'-octachlorobiphenyl, and decachlorobiphenyl and average log K_{ow} values selected from the literature were 2.62 (4,5), 3.38 (4,5), 4.08 (5,6), 5.42 (5,7,8), 6.18 (5,7,9), 7.12 (5,7) and 8.23 (5,7), respectively. For the chemicals with log K_{ow}'s of 6.00 or greater, their values were primarily determined using the "generator column" technique, a National Bureau of Standards method (10) and are the best values, currently available, for chemicals with high log K_{ow}'s.

The correlative relationship was found by regressing the logarithm of the K_{ow} against the logarithm of the corrected retention time (t_c) using an equation of the form:

$$\log K_{ow} = A * \log t_c + B \qquad \text{where } t_c = t_r - t_o$$

where A and B are regression coefficients and t_r and t_o are the retention times for the solute of interest and for an unretained solute, respectively. The retention time of the unretained solute was determined using acetone and/or acetonitrile.

RESULTS AND DISCUSSION

The HPLC estimated log K_{ow}'s for the eight tetrachlorinated planar molecules are listed in Table 1. The average prediction error for the estimation method used here is ca. 0.50 (1).

Table 1. Predicted Log K_{ow}'s for Tetrachlorinated Planar Molecules

	Log K_{ow}[a]		
	$\bar{x}$	s	n
Dibenzo-p-dioxins			
2,3,7,8-	7.02	0.028	2
1,2,3.4-	7.18	0.029	4
1,3,7,9-	7.06	0.021	2
1,3,6,8-	7.20	0.007	2
Dibenzofuran			
2,3,7,8-	5.82	0.017	3
9H-Carbazole			
1,3,6,8-	5.75	0.030	3
Biphenylene			
2,3,6,7-	6.14	0.042	2
Biphenyl			
3,3',4,4'-	5.81	0.049	4

[a] x = mean, s = standard deviation, n = number of determinations.

For comparison purposes, K_{ow}'s estimated using the HPLC technique for chlorinated dibenzofurans and dibenzo-p-dioxins by Sarna et al. (2) are reported in Table 2. However, these values were determined using estimated log K_{ow}'s in the correlative relationship. We have reevaluated the data of Sarna et al. (2) using experimental log K_{ow}'s, displayed in Table 3, rather than estimated log K_{ow}'s in the correlative relationship. After reevaluating the data of Sarna et al. (2), agreement between the log K_{ow}'s determined for the tetrachlorodibenzo-p-dioxins in this investigation and from the reevaluated data of Sarna et al. (2) is excellent (Table 2). In addition, these values (Table 2) suggest that the log K_{ow}'s for the dibenzofurans and dibenzo-p-dioxins range from ca 4.0 for the unsubstituted parent molecule to ca. 8.6 for the octachlorinated molecules.

Table 2. Predicted Log K_{ow}'s for Chlorinated Dibenzofurans and Dibenzo-p-dioxins from Sarna et al. (2) and After Reevaluation of the Data of Sarna et al. (2).

	Log K_{ow}'s Sarna et al. (2)	Log K_{ow}'s Reevaluated Data of Sarna et al. (2)
Dibenzo-p-dioxins		
Unsubstituted	4.46*	4.20**
1-	5.18	4.75
2-	5.64	5.08
2,7-	6.62	5.75
1,2,4-	7.76	6.45
1.2.3,7-	8.60	6.91
1,2,3,4-	8.91	7.08
1,3,6,8-	9.02	7.13
1,2,3,4,7-	9.65	7.44
1.2,3,4.7,8-	10.44	7.79
1,2,3,4,6,7,8-	11.50	8.20
1,2.3.4.5,6,7,8-	12.72	8.60
Dibenzofurans		
Unsubstituted	4.10	3.92
2.8-	5.95	5.30
1,2,3,4,5,6,7,8-	13.37	8.78

* Biosil ODS-10 column and quadratic correlative relationship. **Quadratic correlative relationship employed.

Table 3. Experimental Log K_{ow}'s

Compound	Log K_{ow}	Reference
Catechol	0.95	11
Aniline	0.90	4
Phenol	1.49	4
4-Nitrophenol	1.95	4
Benzene	2.13	11
Toluene	2.63	4
Bromobenzene	2.99	11
Ethylbenzene	3.15	4
1,2 3-Trimethylbenzene	3.66	4
Biphenyl	3.89	7
2-Chlorobiphenyl	4.44	5,7*
Bibenzyl	4.81	11
1,2,3.4-Tetrachlorobenzene	4.65	5.8*
2,4-Dichlorobiphenyl	5.14	7
Pentachlorobenzene	5.03	5
2,4,5-Trichlorobiphenyl	5.66	5,7*
1,2,4,5-Tetrabromobenzene	5.13	4
Hexachlorobenzene	5.47	5
2.3,4,5-Tetrachlorobiphenyl	5.72	5
2,2',4,5,5'-Pentachlorobiphenyl	6.18	5,7,9*
2,2',4.4',5,5'-Hexachlorobiphenyl	6.65	7,9,12*
Decachlorobiphenyl	8.23	5,7*

* Average of literature values.

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